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MECHANICAL PROPERTIES OF STRUCTURAL POLYMERS
(Computer Simulations and Key Experiments)
(A DARPA University Research Initiatives Program)

Final Technical Report
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A. EXECUTIVE SUMMARY

I. INTRODUCTION AND GOALS

In terms of molecular microstructures and morphology, polymers are some of the most complex engineering materials. They offer, however, vast potential in structural applications, in both monolithic form as well as matrices in composite materials. Through chemical synthesis new polymers are being put together routinely in large numbers. In this quest, the understanding of their physical properties and, more seriously, their mechanical properties have lagged behind - often resulting in inadequate exploitation of the full potential of existing polymers. While the physics and chemistry of polymers have received more serious attention, the mechanical properties have been studied largely phenomenologically without adequately relating these properties through the relevant mechanisms to the microstructure or morphology.

To rectify this deficiency and to elucidate the mechanisms that govern the mechanical properties of polymers a long range fundamental investigation was initiated in 1986 through the opportunity offered by the DARPA University Research Initiatives Program. In that investigation several areas were singled out for intensive study by a combination of computer simulation and key experiments. In these the goal was to elucidate the fundamental molecular and morphological mechanisms of large strain deformation in a carefully considered set of polymers which would then have broad application to other polymers having related morphology. The four fundamental tasks that were identified for intensive study were:

1. Molecular level mechanisms of plastic deformation and incipient cavitation in glassy polymers by computer simulation.
2. Molecular level mechanisms that govern the kinetics of structural alterations and relaxations, such as the glass transition in flexible chain polymers.
3. Morphological level processes of plastic flow to very large strains in semi-crystalline polyethylene by computer simulation.
4. Experimental study of texture development in very large strain plastic flow primarily in the compression and shear realm in polyethylene, Nylon, polyethyleneterephthalate and even isotactic polystyrene - to follow in detail the morphological alterations and compare them with the predictions of the computer simulations of Task 3 above.

Operationally these four tasks were each directed by a senior investigator with the principal investigator, Argon acting as the "cement" between the separate tasks. The

four investigators were U.W. Suter, S. Yip, D.M. Parks, and R.E. Cohen respectively for the four tasks.

In nearly all respects the principal goals of the investigation were reached, while in some instances an entire set of materials could not be investigated as initially hoped. On the other hand additional and initially unplanned generic investigations on more model materials were carried out with great success and provided powerful insight. The principal technical accomplishments are listed in Section II below, with references to the relevant publications that have resulted form the research, which have been given in chronological order in Section B. Several additional journal papers and two major summaries of the work are in preparation and will be submitted for publication before the end of the calendar year 1992. In Section C a list of all the persons associated with the program is given.

II. SUMMARY OF MAJOR ACCOMPLISHMENTS

- Extensive study of the dynamic structural properties of model 2-D atomic glasses by molecular dynamics and the modelling of the mechanisms of plastic deformation in it (2-5).
- Modelling of structural relaxations, and plastic deformation, their kinematical features and kinetics by a Monte Carlo technique based on Eshelby transformations. (27;29-31).
- Simulation of the structure of PC; the kinematics and energetics of phenylene ring flips and carbonate group rotations (17-19).
- Small strain elastic properties and large strain plastic deformation of glassy PC (28).
- Simulation of plastic flow and its molecular level kinematics in polypropylene elucidating the very cooperative nature of unit plastic events (14;21;23-25;37).
- Simulation of inelastic dilatation of polypropylene as a precursor for craze initiation (25;28).
- Fully flexible molecular dynamics model simulating structural relaxations under constant pressure and temperature in polypropylene (9).
- Topological features of a glass transition in polypropylene, leading to a radically new interpretation (in preparation).
- Development of a new formalism of micromechanics of constrained deformation of large assemblies of lamellar polycrystals with associated amorphous layers. Prediction of realistic deformation textures in PE, and Nylon 6. New formalism has wide applicability to also hexagonal and other crystals with constrained deformation (8;10-12;35-36).

- Development of the means of obtaining highly oriented semi-crystalline polymers (Nylon, PE, PET) in bulk. Determination of the yield surfaces of highly textured (quasi single crystal) Nylon and PE for use in computer codes. New insight into formation of long periods in PE (7;15;16;20;32-34;36).
- Elastic properties of highly textured Nylon (20).
- Morphological alteration in plane strain compression, uniaxial compression, and simple shear in PE and Nylon leading to texture evolution (7;15;16;20;32-34;36).
- Anisotropic plastic properties of highly textured Nylon (20).
- Plastic deformation and early texture evolution in isotactic PS (in preparation).
- Dislocation mechanisms of plastic shear in quasi-crystalline highly oriented PE and Nylon-6 (in preparation).

B. PUBLICATIONS

I. REFEREED PAPERS IN JOURNALS AND CONFERENCE PROCEEDINGS

1. M.C. Boyce, D.M. Parks and A.S. Argon, "Plastic Flow in Oriented Glassy Polymers," *Intern. J. Plasticity*, **5**, 593 (1989).
2. D. Deng, A.S. Argon, and S. Yip, "A Molecular Dynamics Model of Melting and Glass Transition in an Idealized Two-Dimensional Material-I," *Phil. Trans. Royal Society*, **A329**, 549 (1989).
3. D. Deng, A.S. Argon, and S. Yip, "Topological Features of Structural Relaxations in a Two-Dimensional Model Atomic Glass-II," *Phil. Trans. Royal Society*, **A329**, 575 (1989).
4. D. Deng, A.S. Argon, and S. Yip, "Kinetics of Structural Relaxations in a Two-Dimensional Model Atomic Glass-III," *Phil. Trans. Royal Society*, **A329**, 595 (1989).
5. D. Deng, A.S. Argon, and S. Yip, "Simulation of Plastic Deformation in a Two-Dimensional Model Atomic Glass by Molecular Dynamics-IV," *Phil. Trans. Royal Society*, **A329**, 619 (1989).
6. M.C. Boyce, G.G. Weber, and D.M. Parks, "On the Kinematics of Finite Strain Plasticity", *J. Mech. and Phys. of Solids*, **37**, 647 (1989).
7. H.H. Song, R.E. Cohen and A.S. Argon, "Morphology of Highly Oriented HDPE," *Macromolecules*, **23**, 870 (1990).
8. D.M. Parks and S. Ahzi, "Polycrystalline Plastic Deformation and Texture Evolution for Crystals Lacking Five Independent Slip Systems," *J. Mech. and Phys. of Solids*, **38**, 701 (1990).

9. M.F. Sylvester, S. Yip and A.S. Argon, "Investigation of Structural and Dynamic Differences in the Glassy and Liquid States of Atactic Polypropylene in "Computer Simulation of Polymers", edited by R.J. Roe (ACS: Washington, D.C.) p. 105 (1991).
10. S. Ahzi, D.M. Parks, and A.S. Argon, "Modeling of Plastic Deformation and Evolution of Anisotropy in Semi-Crystalline Polymers," in "Computer Modeling and Simulation of Manufacturing Processes", edited by B. Singh, Y.T. Im, I. Haque and C. Altan (ASME: New York) Md-Vol 20, Book NO. G00552, p. 287 (1990).
11. D.M. Parks and S. Ahzi, "Micromechanical Modeling of Plasticity and Texture Evolution in Semi-Crystalline Polymers", in "Inelastic Deformation of Composite Materials" edited by G.J. Dvorak, (Springer: New York) 325 (1991).
12. S. Ahzi, D.M. Parks, and A.S. Argon, "Modeling of Deformation Textures in Semi-Crystalline Polymers", "Proc. 9th International Conference on Textures of Materials", ICOTOM-9: Avignon (1990).
13. A.S. Argon, "Inelastic Deformation and Fracture of Glassy Solids", in "Materials Science and Technology", edited by R.W. Cahn, P. Haasen, and E.J. Kramer, (VCH: Weinheim, Germany) (vol. editor H. Mughrabi) Vol. 6, in the press (1992).
14. A.S. Argon, M. Hutnik, P. Mott and U.W. Suter, "The Molecular View of Plastic Deformation and Precursor Processes of Crazing in Glassy Polypropylene and Polycarbonate", in "Deformation, Yield and Fracture of Polymers - VIII", (Plastics and Rubber Institute: London), p. 1-1 (1991).
15. A. Galeski, A.S. Argon, and R.E. Cohen, "Deconvolution of X-ray Diffraction Data to Elucidate Plastic Deformation Mechanisms in the Uniaxial Extension of Bulk Nylon 6", *Macromolecules*, **24**, 3945 (1991).
16. A. Galeski, A.S. Argon, and R.E. Cohen, "Morphology of Bulk Nylon 6 Subjected to Plane Strain Compression", *Macromolecules*, **24**, 3953 (1991).
17. M. Hutnik, A.S. Argon, and U.W. Suter, "Conformational Characterization of the Polycarbonate of 4,4'-Isopropyledene-diphenol", *Macromolecules*, **24**, 5956 (1991).
18. M. Hutnik, F.T. Gentile, P.J. Ludovice, U.W. Suter, and A.S. Argon, "An Atomistic Model of the Amorphous Glassy Polycarbonate of 4,4'-Isopropyledene-diphenol", *Macromolecules*, **24**, 5962 (1991).
19. M. Hutnik, A.S. Argon, and U.W. Suter, "Quasi-Static Modeling of Chain Dynamics in the Amorphous Glassy Polycarbonate of 4,4'-Isopropyledene-diphenol", *Macromolecules*, **24**, 5970 (1991).
20. L. Lin and A.S. Argon, "Deformation Resistance in Oriented Nylon 6", *Macromolecules*, **25**, 4011 (1992).

21. P.H. Mott, A.S. Argon, and U.W. Suter, "The Atomic Strain Tensor", *J. Computational Phys.*, **101**, 140 (1992).

22. Z. Bartczak, R.E. Cohen and A.S. Argon, "Evolution of the Crystalline Texture of High-Density Polyethylene during Uniaxial Compression", *Macromolecules*, **25**, 4692 (1992).

23. A.S. Argon, P.H. Mott, and U.W. Suter, "Simulation of Plastic Deformations in a Flexible Chain Glassy Polymer", *Phys. Stat. Sol.*, **172**, 193 (1992).

24. A.S. Argon, P.H. Mott, and U.W. Suter, "Mechanisms of Plastic Flow in a Flexible Chain Glassy Polymer", in "Modeling of Plastic Deformation and its Engineering Applications", edited by. S.I. Andersen, J.B. Bilde-Sorensen, N. Hansen, D. Juul Jensen, T. Leffers, H. Lilholt, T. Lorentzen, O.B. Pedersen and B. Ralph, (Riso National Laboratory: Roskilde, Denmark), 1 (1992).

25. P.H. Mott, A.S. Argon, and U.W. Suter, "Simulation of Dilatation in Flexible Chain Glassy Polymers", in "Modeling of Plastic Deformation and its Engineering Applications", edited by. S.I. Andersen, J.B. Bilde-Soresen, N. Hansen, D. Juul Jensen, T. Leffers, H. Lilholt, T. Lorentzen, O.B. Pedersen and B. Ralph, (Riso National Laboratory: Roskilde, Denmark), 361 (1992).

26. V.V. Bulatov, and A.S. Argon, "Atomistic vs. Continuum Modelling of Plastic Flow in an Idealized 2-D Solid", in "Modeling of Plastic Deformation and its Engineering Applications", edited by. S.I. Andersen, J.B. Bilde-Soresen, N. Hansen, D. Juul Jensen, T. Leffers, H. Lilholt, T. Lorentzen, O.B. Pedersen and B. Ralph, (Riso National Laboratory: Roskilde, Denmark), 227 (1992).

27. V.V. Bulatov, and A.S. Argon, "A Method for Identification of the Core of Inelastic Events in Atomistic Computer Models", *Phys. Rev.*, **A46**, in the press (1992).

28. M. Hutnik, A.S. Argon, and U.W. Suter, "Simulation of Elastic and Plastic Response in Glassy Polycarbonate of 4,4'-Isopropyledene-diphenol", *Macromolecules*, in the press.

29. V.V. Bulatov, and A.S. Argon, "A Stochastic Model of Continuum Elasto-Plastic Behavior, I. Numerical Approach and Strain Localization", *Acta Metall. et Mater.*, submitted for publication.

30. V.V. Bulatov, and A.S. Argon, "A Stochastic Model of Continuum Elasto-Plastic Behavior, II. Study of Glass Transition and Structural Relaxation", *Acta Metall. et Mater.*, submitted for publication.

31. V.V. Bulatov, and A.S. Argon, "A Stochastic Model of Continuum Elasto-Plastic Behavior, III. Plasticity in Ordered vs. Disordered Solids", *Acta Metall. et Mater.*, submitted for publication.

32. A. Galeski, Z. Bartczak, A.S. Argon and R.E. Cohen, "Morphological Alterations during Texture-Producing Plastic Plane Strain Compression of High Density Polyethylene", *Macromolecules*, in the press.
33. Z. Bartczak, A.S. Argon and R.E. Cohen, "Deformation Mechanisms in Single Crystal Textured High Density Polyethylene", *Macromolecules*, **25**, 5036 (1992).
34. Z. Bartczak, A.S. Argon and R.E. Cohen, "Texture Evolution during Plastic Deformation of High Density Polyethylene by Simple Shear", *Macromolecules*, submitted for publication.
35. B.J. Lee, D.M. Parks, and S. Ahzi, "Large Strain Plastic Deformation in High Density Polyethylene", *J. Mech. Phys. Solids*, submitted for publication.
36. B.J. Lee, A.S. Argon, D.M. Parks, S. Ahzi and Z. Bartczak, "Simulations of Large Plastic Deformation and Texture Evolution in High Density Polyethylene", *Macromolecules*, submitted for publication.
37. P.H. Mott, A.S. Argon, and U.W. Suter, "Atomistic Modeling of Plastic Deformation of Glassy Polymers", *Phil Mag.*, in the press.
38. P.H. Mott, A.S. Argon, and U.W. Suter, "Atomistic Modeling of Cavitation of Glassy Polymers", *Phil Mag.*, submitted for publication.
39. L. Lin and A.S. Argon, "Structure and Plastic Deformation of Polyethylene: A Review", *J. Mater. Sci.*, submitted for publication.
40. A. Bellare, R.E. Cohen and A.S. Argon, "Development of Texture in PET by Plane Strain Compression", *Polymer*, in the press.

II. ABSTRACTS OF ORAL PRESENTATIONS
(for invited and contributed talks in national and international conferences)

1. M. Hutnik and U.W. Suter, "A Rotational Isomeric State Model for the Polycarbonate of 2,2'-Bis4-Hydroxyphenyl Propane", *Polymer Preprints*, **28-2**, 293 (1987).
2. J.K. Anderson, R.E. Cohen and A.S. Argon, "Deformation Behavior of Isotactic Polystyrene", *Polymer Preprints*, **29-2**, 165 (1988).
3. S. Ahzi, D.M. Parks, and A.S. Argon, "Simulation of Texture Evolution in Deformed Semi-Crystalline Polymers", TMS/AIME Symposium on Modeling of Anisotropic Material Behavior in Chicago, IL, Sept. 25 (1988).
4. D.M. Parks, S. Ahzi, "Micromechanical Modelling of Deformation and Texture Evolution in Semi-Crystalline Polymers", *Bull. Amer. Phys. Soc.*, **34**, 435 (1989).
5. S. Ahzi, H.H. Song, D.M. Parks, R.E. Cohen and A.S. Argon, "Simulation

of Texture Evolution in Deformed Polyethylene", *Bull. Amer. Phys. Soc.*, **34**, 435 (1989).

6. H.H. Song, R.E. Cohen and A.S. Argon, "Simulation of Highly Oriented HDPE Obtained via Rolling and Channel Die Compression", *Bull. Amer. Phys. Soc.*, **34**, 436 (1989).
7. J.K. Anderson, R.E. Cohen and A.S. Argon, "Deformation Studies of Isotactic Polystyrene", *Bull. Amer. Phys. Soc.*, **34**, 706 (1989).
8. M.F. Sylvester, S. Yip, and A.S. Argon, "Molecular Dynamics Simulation of a Relaxed Polymer Glass: Structural Differences Between the Glass and Liquid States", *Bull. Amer. Phys. Soc.*, **34**, 710 (1989).
9. M. Hutnik, A.S. Argon and U.W. Suter, "Molecular Structure of Amorphous Bisphenol-A Polycarbonate", *Polymer Preprints*, **30-2**, 36 (1989).
10. M.F. Sylvester, S. Yip, and A.S. Argon, "Molecular Dynamics Simulation of Atactic Polypropylene: Structural Differences Between the Liquid and Glassy States", *Polymer Preprints*, **30-2**, 32 (1989).
11. S. Ahzi, D.M. Parks, and A.S. Argon, "Simulation of Deformation Texture Evolution in Semi-Crystalline Polymers", *Polymer Preprints*, **30-2**, 55 (1989).
12. P.H. Mott, A.S. Argon, and U.W. Suter, "Plastic Deformation of Glassy Polypropylene: The Molecular View", *Polymer Preprints*, **30-2**, 34 (1989).
13. S. Ahzi, D.M. Parks, and A.S. Argon, "Simulation of Texture Evolution in Deformed Semi-Crystalline Polymers", ASM Symposium on Textures in Non-Metallic Materials in Indianapolis, Oct. 2 (1989).
14. A.S. Argon, M. Hutnik, P.H. Mott, and U.W. Suter, "Simulation of Inelastic Deformation in Glassy Polypropylene and Polycarbonate", *Polymer Preprints*, **31-1**, 689 (1990).
15. P.H. Mott, A.S. Argon, and U.W. Suter, "Simulation of Large Deformation in Glassy Atactic Polypropylene", MRS Symposium on Structure, Relaxation and Physical Aging of Glassy Polymers, Boston, December (1990).
16. M. Hutnik, A.S. Argon, and U.W. Suter, "Simulation of the Structure of Dense, Amorphous Bisphenol-A-Polycarbonate", MRS Symposium on Structure, Relaxation and Physical Aging of Glassy Polymers, Boston, December (1990).
17. P.H. Mott, A.S. Argon, and U.W. Suter, "Kinematics of Plastic Deformation in Atactic, Glassy Polypropylene ", *Polymer Preprints*, **33-1**, 619 (1992).
18. V.V. Bulatov and A.S. Argon, "Monte Carlo Simulation of Structure and Plasticity in Disordered Solids", *Polymer Preprints*, **33-1**, 588 (1992).
19. M. Sylvester, "Simulation of Dynamic Properties of Polypropylene", NATO

Research Workshop on Computer Simulation at Bath University, England, Sept. 4 (1988).

(Many other unlisted invited talks were given at Universities etc. throughout the duration of the Program. These have not been listed.)

III. DOCTORAL THESES

1. J.K. Anderson-Rakestraw, "Deformation Behavior of a Model Semi-Crystalline Polymer: Studies of Isotactic Polystyrene", Dept. of Chemical Engineering, MIT, June 1990.
2. A. Bellare, "Deformation Induced Texture Development in Polyehtylene-Terephthalate", Dept. of Chemical Engineering, MIT, October 1991.
3. M. Hutnik, "Simulation of the Structure and Inelastic Behavior of Dense, Amorphous Bisphenol-A Polycarbonate", Dept. of Materials Science and Engineering, MIT, June 1991.
4. L. Lin, "An Experimental Study of Deformation Mechanisms and Resistance of Semi-Crystalline Polymers", Dept. of Mechanical Engineering, MIT, June 1991.
5. P.H. Mott, "Atomistic Modeling of Deformation of Glassy, Atactic Polypropylene", Dept. of Materials Science and Engineering, MIT, February 1992.
6. M.F. Sylvester, "Molecular Dynamics Studies of the Liquid Glass Transition in Atactic Polypropylene", Dept. of Mechanical Engineering, MIT, June 1992.

C. PERSONS ASSOCIATED WITH THE PROGRAM

I. FACULTY

Ali S. Argon	P.I.
Robert E. Cohen	Task IV
David M. Parks	Task III
Ulrich W. Suter	Task I
Sidney Yip	Task II

II. POST DOCTORAL WORKERS

Said Ahzi	Task III	(1987-1991)
Zbigniew Bartczak	Task IV	(1989-1991)
Charles Berney	Task IV	(1987, 1990)
Mary C. Boyce	Task III	(1987)
Bing Jean Lee	Task III	(1991-1992)
Li Lin	Task IV	(1991-1992)
Hyun H. Song	Task IV	(1987-1989)

III. VISITING SCIENTISTS

Vasily V. Bulatov	Tasks I & II	(1990-1992)
Degue Deng	Tasks I & II	(1986-1987; 1991)
Andrzej Galeski	Task IV	(1987, 1989, 1990)
Eva P. Galeska	Task IV	(1987)
Gunther Weymans	Task I	(1987)

IV. GRADUATE STUDENTS (DOCTORAL)

Julie A.:derson-Rakestraw	Task IV	(1986-1990)
Anuj Bellare	Task IV	(1987-1991)
Michelle Hutnik	Task I	(1987-1991)
Li Lin	Task IV	(1987-1988)
Mohammadali Moghimi	Task II	(1987)
Peter H. Mott	Task I	(1989-1992)
Mark F. Sylvester	Task II	(1987-1992)
Meng-J. Wang	Task II	(1987)

V. UNDERGRADUATE STUDENTS

Anthony Cooper	Task IV	(1989-1990)
Josephine H-W Cheng	Task IV	(1987)